Kondo Effect and Spin Glass Behavior of Dilute Iron Clusters in Silver Studied by Mössbauer Spectroscopy and Resistivity

W. T. Herrera*

Instituto de Física, Universidade do Estado de Rio de Janeiro,
Rua São Francisco Xavier 524, 20559-900, RJ, Brazil

S. M. Ramos and E. M. Baggio-Saitovitch

Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, 22290-180, RJ, Brazil

F. J. Litterst

Institute for Physics of Condensed Matter, Technische Universität Braunschweig,
Mendelssohnstrasse 3, 38106 Braunschweig, Germany

Thin films of silver containing $0.3 - 1.5$ at $\%$ Fe have been prepared by vapor co-deposition. Depending on substrate temperature and iron concentration we could systematically follow the formation of nanometer size clusters of iron from initially dilute iron monomers. samples were characterized via X-ray diffraction, resistivity and Mössbauer spectroscopic measurements.

The magnetic behavior derived from Mössbauer data can be best described with an ensemble of ferromagnetic mono-domain particles. The magnetic freezing observed at low temperatures, is controlled via the inter-particle interactions mediated via conduction electron polarization, i.e. $RKKY$ interaction.

The interaction of the cluster magnetic moments with the conduction electron sea is best quantified by the electrical resistivity data. For all studied concentrations we find a non-monotonic variation with temperature which can be understood by competing shielding of the cluster moments by conduction electron spin scattering due to Kondo effect and the magnetic coupling.

I. INTRODUCTION

In the past Fe precipitates in noble metals have been studied following various tracks of preparation. Mostly precipitates are formed from concentrated solid solutions under thermal treatment. Less common is starting out from very dilute Fe impurities embedded in the metal host and subsequent annealing leading to diffusion of impurities and clustering. For characterizing the electronic state of Fe in these precipitates and its magnetic properties Mössbauer spectroscopy is a highly suitable method.

Of particular interest are systems with very low miscibility in solid and liquid state, like e.g. $Ag{:}Fe$. Even very dilute alloys with low concentration of Fe in Ag may only be achieved via non-equilibrium preparation, i.e. vapor deposition[1,2,3], electron-beam co-evaporation[4], mechanical alloying[5] or implantation[6,7]. Well known are the early Mössbauer spectroscopic studies of ppm concentrations of Fe in Ag prepared via diffusion of ^{57}Co into the host matrix with the radioactive decay of ^{57}Co leading to ^{57}Fe[8].

Morales et al[1] succeeded in preparing films in the range of percent concentration of Fe in Ag by evaporating the elements in proper proportion and co-depositing them onto Kapton substrates kept at 16 K. From the Mössbauer spectra isolated monomeric and dimeric Fe in the Ag matrix could be clearly identified as major components. In addition minor contribution was found which was attributed to clusters of fcc iron.

Upon annealing at room temperature the formation of clusters is enhanced, but only for annealing around 480 K bcc Fe precipitates are formed. An identification of the various species is possible from their distinctly different hyperfine parameters.

II. EXPERIMENTAL

In continuation of these studies we prepared films by co-deposition of Fe and Ag with nominal concentrations between 0.3 and 1.5 at $\%$ of Fe. We have characterized the samples by X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and electrical resistivity measurements. In order to receive a sufficient amount of ^{57}Fe for performing Mössbauer experiments we used iron metal enriched to 90% of ^{57}Fe. The preparation procedure and the evaporation facility were the same as described in refs.[1,2,3]. The base vacuum pressure in the deposition chamber was 2×10^{-9} $mbar$, increasing to 2×10^{-8} $mbar$ during deposition. The films were deposited onto Kapton foils kept either at 285 K or 85 K. The deposition rate was monitored using piezo-crystals and typical values were 4 Å$/s$ for Ag and 0.02 Å$/s$ for Fe (see table I). The total film thicknesses were typically 1000 to 4000 nm. Under these preparation conditions we expected clusters to be formed directly during the deposition process and not only after annealing.

First sets of Mössbauer experiments were performed in situ, i.e. in the cryostat where the preparation was done. The spectrometer was of standard type with sinusoidal velocity sweep. The $^{57}CoRh$ source was kept at room temperature. It turned out that the films could be transferred to a variable temperature cryostat ($1.5 K - 300 K$)

without observing any change of the spectra. So it was possible to perform ex situ experiments without inducing structural changes of the film.

Resistivity measurements were taken between 1.5 K and 300 K using a standard 4 contacts technique. X-ray diffraction was performed on a Rigaku MiniFlex using $Cu\ K_{\alpha 1}$ and $K_{\alpha 2}$.

at % Fe	η_{Fe} (Å/s)	η_{Ag} (Å/s)	$T_s(K)$	t (min)	ξ (nm)
0.3	0.009	4.0	285	120	≈ 2886
0.5	0.01	3.0	285	115	≈ 2076
0.8	0.007	1.3	285	124	≈ 972
1.0	0.028	4.05	283	117	≈ 2862
1.2	0.031	1.55	283	120	≈ 1138
1.5	0.035	4.6	280	130	≈ 3615
1.0	0.02	4.5	85	124	≈ 3349
0.4	0.01	3.9	85	140	≈ 3307
0.0	0.0	3.0	285	140	≈ 2322

TABLE I: η deposition rate, T_s substrate temperature, t deposition time and ξ thickness.

III. RESULTS AND DISCUSSION

X-ray diffraction of the iron doped films revealed significant broadenings of the silver Bragg peaks indicating the formation of small grains. Using the Scherrer formula we estimate mean grain sizes of about 22 nm and 11 nm for films deposited onto 285 K and 85 K substrates, respectively. All films reveal a high degree of texture (see fig. 1).

Fig. 2 it shows a series of Mössbauer spectra taken at 300 K for various concentrations of iron in films prepared at 285 K. Below 1 $at\ \%\ Fe$ the spectra are composed by a superposition of three subspectra. One singlet line S can be identified as being caused by iron monomers[1,6,9,10]; we observe in addition two quadrupole split doublets which for all concentrations have practically the same hyperfine parameters. In contrast to the earlier samples prepared by vapor quenching onto substrates kept at $16K$[1], we find no resolved contribution from iron dimers. There is also no indication for the presence of fcc clusters of the type that was found after deposition at low temperatures. We therefore performed a re-analysis of these earlier data and it turned out that they are even better adjusted by the monomer, the dimer and the same two doublet contributions as found for the new samples.

We label these two doublets with DI and DII. The hyperfine parameters and the variation of their relative intensities for the three species are shown in figure 3. The relative amount of monomers is continuously decreasing with increasing iron concentration and finally for more than 1 $at\ \%\ Fe$ the singlet sub-spectrum can be no more
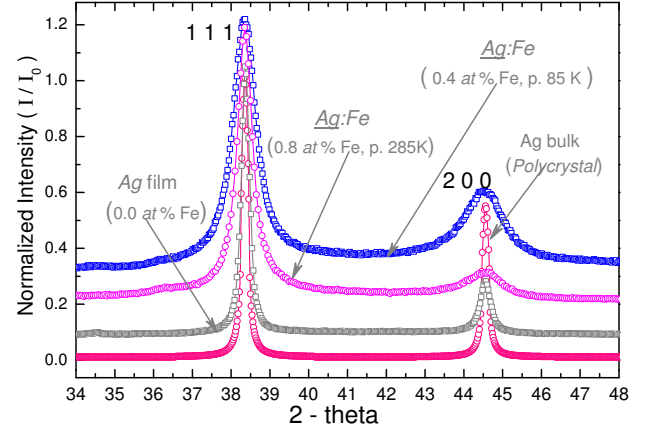

FIG. 1: X-ray diffraction of polycrystalline Ag, a pure Ag film and iron doped Ag films deposited onto 285 K and 85 K substrates.
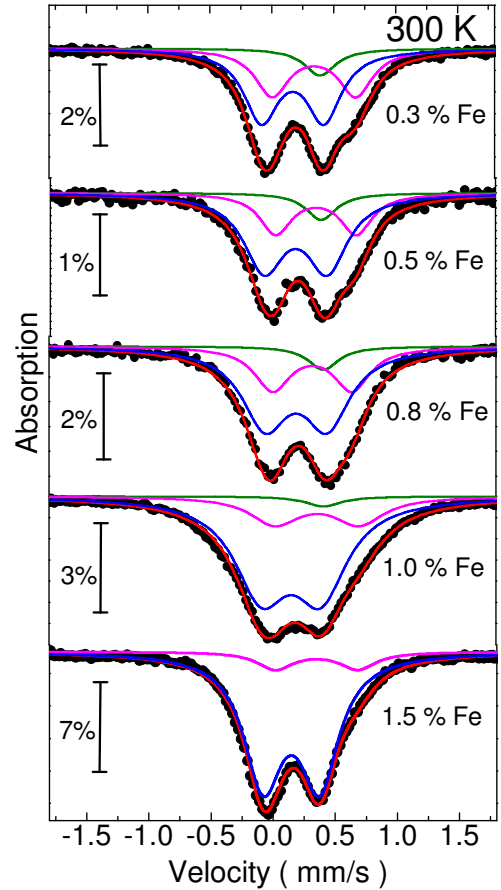

FIG. 2: Mössbauer spectra taken at 300 K for 0.3, 0.5, 0.8, 1.0 and 1.5 $at\ \%\ Fe$.

traced and only a superposition of the two quadrupole doublets is found (fig. 2).

Whereas the relative spectral area of DI is decreasing with increasing iron concentration, the area of DII is increasing. A close lying possible interpretation for the two doublets would be to attribute them to iron on the sur-
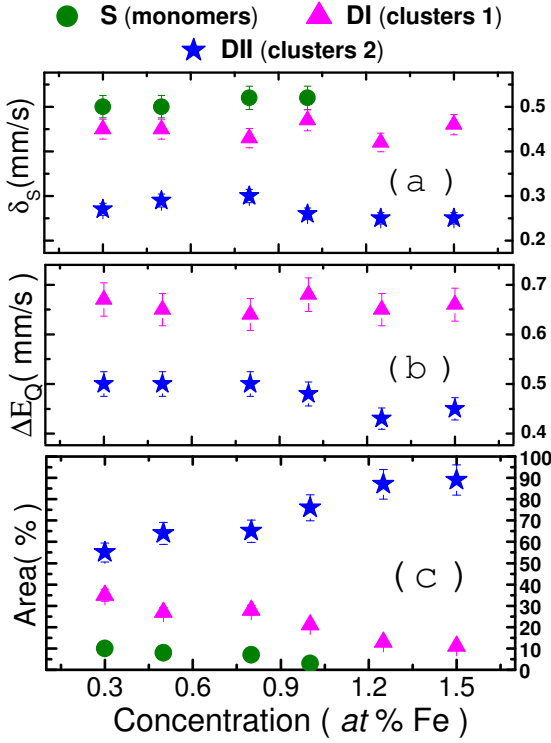
FIG. 3: Hyperfine parameters. (a) isomer shift δ_S, (b) quadrupole splitting ΔE_Q, and (c) relative spectral areas of the subspectra S (monomers), DI and DII (clusters).

FIG. 4: Clusters with 6 and 15 atoms.

FIG. 5: Mössbauer spectra taken at 300 K and 4.2 K for 0.3, 0.5, 0.8, 1.0 and 1.5 $at \% Fe$.

face and from the core of one type of cluster. From the variation of relative areas with concentration one then would have to relate DI to the surface and DII to the core which however would imply cluster sizes in the micrometer range. This definitively can be excluded since such clusters should have fcc or bcc structure and reveal magnetic blocking in the 100 K range or even higher what is not observed (see below).

We attribute the two doublets to clusters in the nanometer range, with DI representing smaller and DII bigger clusters. DI has the higher isomer shift rather close to the value of the monomer and a big quadrupole splitting indicative for a low symmetry surrounding. The isomer shift for DII is smaller meaning that the number of iron neighbors is higher; the quadrupole splitting is smaller, i.e. coming closer to a cubic arrangement. Such clusters are supposed not to fit into the fcc lattice of silver and should appear at grain boundaries especially in view of the small grain structure of our films.

As tentative model one could consider some stable free iron clusters as proposed from theoretical calculations by Rollman et al^{11}, e.g. clusters Fe_6 and Fe_{15} (to see fig. 4). Note that these clusters are so small that practically all iron atoms are on surfaces and the spectral contribution from the core of the particles is zero or negligible.

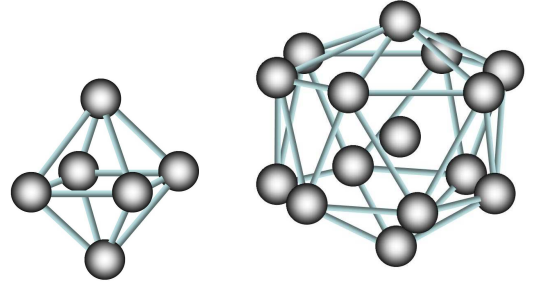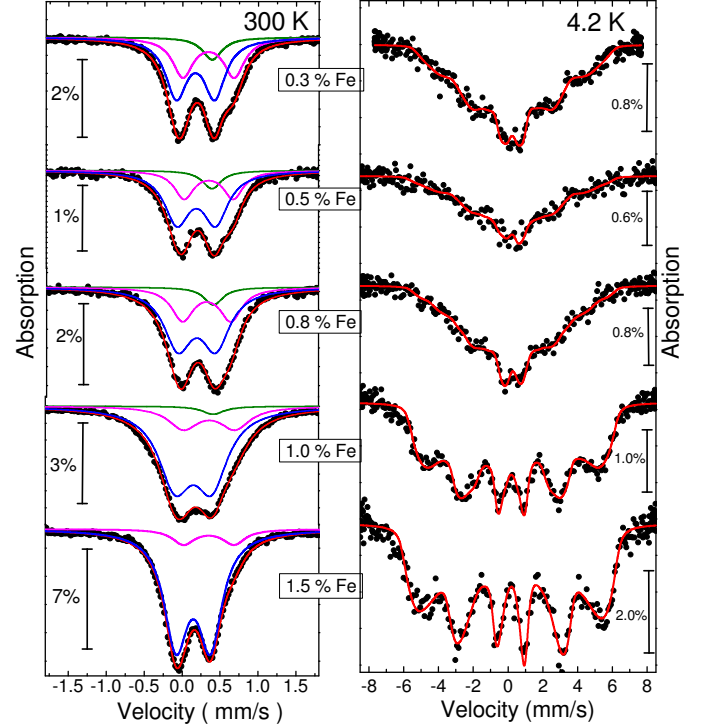For temperatures below about 15 K we find an onset of magnetic hyperfine interaction connected with the freezing of the magnetic moments of the clusters. The spectra taken at 4.2 K are shown in fig. 5. It is clearly seen that there is a distribution of the magnetic hyperfine interaction which becomes better defined with increasing iron concentration, i.e. with larger number of clusters. The drawn lines through the data points of the spectra are simplistic fits using a distribution of hyperfine fields. For the present discussion it may suffice to notice the onset of magnetic interaction. A more detailed interpretation of these patterns (e.g. taking into account the role played by magnetic fluctuations, cluster-cluster interactions etc.) will be presented elsewhere together with susceptibility, magnetization and Mössbauer measurements in applied magnetic field over a wide temperature range. These data yield further support for small clusters with
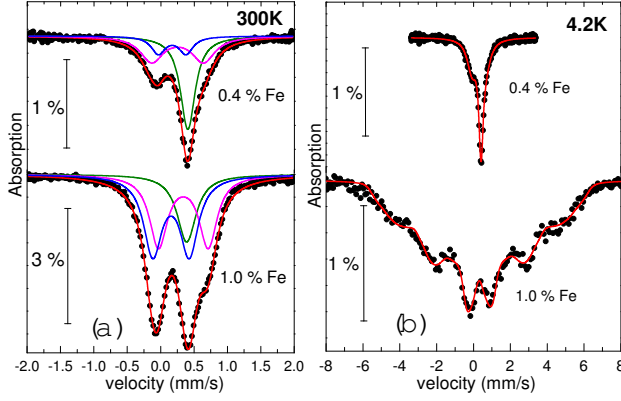
FIG. 6: Mössbauer spectra taken at 300 K and 4.2 K for 0.4 and 1.0 at % Fe (samples prepared at 85K).

moments on the order of about $20 - 50\ \mu_B$.

The room temperature spectra of the samples prepared at 85 K reveal the same three species S, DI and DII, yet with a clearly higher contribution by the monomer S (see fig. 6). At 4.2 K the sample with 1.0 at % Fe shows a magnetic hyperfine pattern which however indicates a lower degree of freezing than found for the sample prepared at 285 K. For the sample with 0.4 at % Fe there is still no indication of a magnetic hyperfine interaction (fig. 6) at 4.2 K.

When comparing the freezing behaviour one has to take into account that the concentration of clusters in the samples prepared at 295 K (with dominant bigger clusters) is in fact lower than in the samples prepared at 85 K, so their distances are larger than those between the isolated monomers for the same nominal concentration of iron. Their interaction however, is increased due to the augmented moment of each cluster and one can thus understand the stronger tendency for freezing with increasing concentration despite longer distances between clusters. Using a RKKY model adopted for clusters[12] with the known Fermi surface vectors of silver and ferromagnetic cluster moments with about 40 μ_B we arrive for our concentrations at average cluster-cluster interaction energies corresponding to $10 - 20\ K$. This is in agreement with the freezing temperatures derived from the Mössbauer data.

The resistivity results for the samples prepared at $285K$ and $85K$ are shown in the Fig. 7 and Fig. 8, respectively. For low iron concentrations we find clear minima in the temperature dependence of the resistivity (typically around 20 K) followed by maxima at lower temperatures. The minima are indicative for the onset of Kondo effect. The typical logarithmic increase of resistivity with decreasing temperature may most clearly be traced for the samples with low concentrations, i.e. with a high number of monomers. Saturation is only achieved below about 2 K which is in agreement with earlier data obtained by Mössbauer[8], TDPAC[13,14] and susceptibility[15] measurements on Fe monomers in bulk
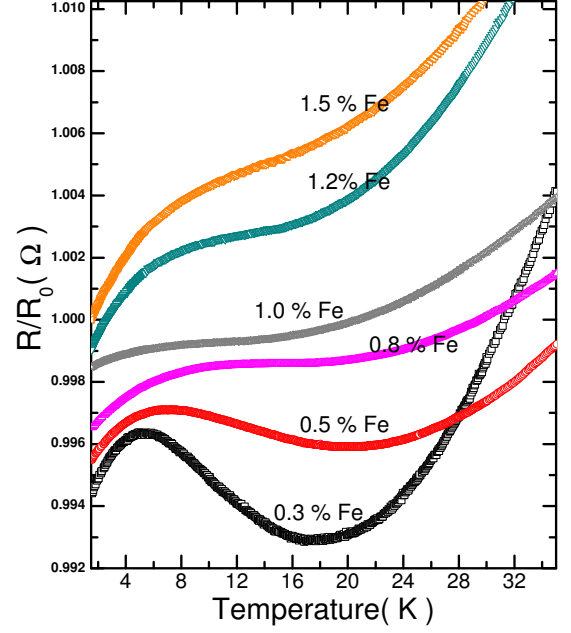

FIG. 7: Electrical resistivity for 0.3, 0.5, 0.8, 1.0, 1.2 and 1.5 at % Fe prepared at 285K, normalized to R_0 ($T = 1.5K$)
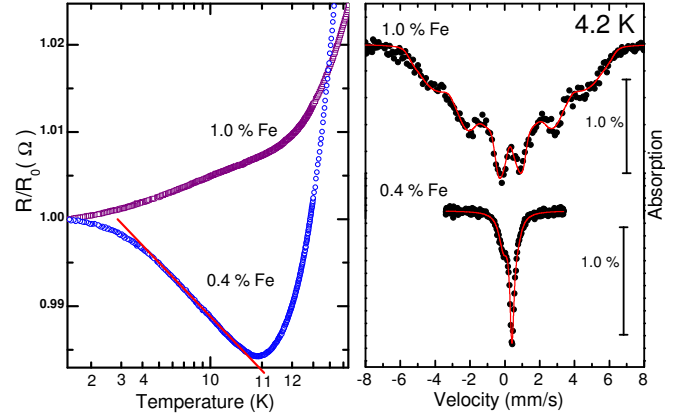

FIG. 8: Electrical resistivity for 0.4 and 1.0 at % Fe prepared at 85K, normalized to R_0 ($T = 1.5K$).

silver where Kondo temperatures of about $1.5 - 2\ K$ were found.

Actually an increased value was derived from TDPAC[16] for dilute iron impurities in nanocrystalline silver. This discrepancy of T_K found between bulk and nanocrystalline silver was attributed to a pressure induced increased hybridization of iron $3d$ electrons with the conduction electrons near the grain surfaces[17,18]. The silver grain size of 19 nm is actually nearly the same as found for our samples prepared at 285 K with grain sizes of about 22 nm, however, our data do not support an increase of Kondo temperature.

The mentioned resistivity maxima are observed for samples containing a higher amount of clusters and also
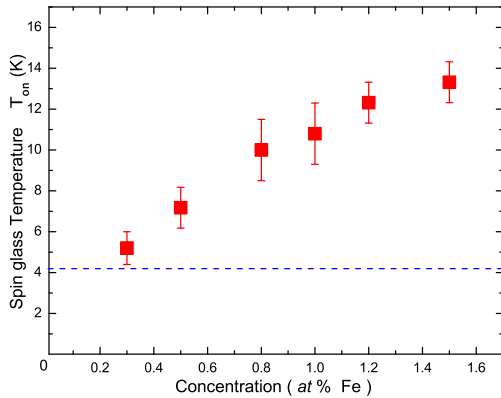
FIG. 9: Onset temperature T_{on} for spin freezing derived from resistivity data.

revealing spin freezing from Mössbauer effect. The decrease of resistivity for temperatures below the maxima is related to the onset of the magnetic interaction between the clusters. It is getting clearly stronger with increasing concentration of iron, i.e. also with number of clusters. The shape of the resistivity curves are in very good qualitative agreement with the calculations of Larsen[19] and more recently by Vavilov et al[20] predicting a non monotonic variation of resistivity with temperature when in concentrated systems the RKKY interaction between magnetic impurities is strong compared to the Kondo interaction. Similar observations have been reported, e.g., for Au and Cu matrices doped with Mn and Fe impurities, there however at much lower concentrations[21]. For concentrations above about 1 at % Fe the resistivity minimum can no more clearly be traced in our data and only the turn-down of resistivity due to the magnetic freezing is visible. Despite the temperature where the maximum of resistivity occurs does not directly correspond to the spin glass temperatures as derived e.g. from the susceptibility cusp (see refs.[19,21]), we plot this temperature T_{on} in fig. 9 for demonstrating the concentration dependence of spin freezing. The values were obtained from the first derivative for 0.3, 0.5 and 0.8 at % Fe and from the second derivate for 1.0, 1.2 and 1.5 at %. A straight line

in fig. 9 indicates the $T = 4.2$ K the temperature at which the Mössbauer measurements were taken. This illustrates why the spectra for $Fe < 1.0$ at % are not static since the freezing is very close to 4.2 K.

For the higher concentrations we take the temperatures where the downturn of resistivity from the phonon contribution becomes apparent. These values between about 5 and 15 K are again in fair agreement with the observed onset of magnetic hyperfine interaction from the Mössbauer data for these concentrations. The disappearance of the Kondo minimum occurs in parallel to the vanishing of the monomer contribution in the Mössbauer spectra and also of the clusters of type DI. There is no clear indication for Kondo scattering when clusters of type DII become dominant. We therefore have to conclude that the Kondo anomalies observed in the resistivity data are mainly caused by contributions from monomeric iron and eventually of clusters DI. In any case the Kondo temperatures for samples with iron concentrations above about 1 at % must to be below about 3 K.

IV. CONCLUSIONS

In summary we have observed the formation of well defined nano-sized iron clusters in silver films prepared by co-deposition from iron and silver atomic beams under varying conditions and for a series of concentrations. Resistivity data give clear evidence for Kondo effect for samples containing monomeric iron impurities and clusters of type DI but not for clusters of type DII, i.e for iron concentrations up to about 1 at %. Samples containing clusters reveal the typical non-monotonic resistivity behaviour expected for spin glass freezing competing with Kondo effect. The spin glass freezing is clearly visible from the appearance of magnetic hyperfine splitting. The spin glass transition temperature is in good agreement with estimates from a RKKY model for interacting clusters.

* Electronic address: william@cbpf.br
[1] M. A. Morales, E. C. Passamani, E. Baggio-Saitovitch, Phys. Rev. B **66**, 144422, (2002).
[2] C. Larica, E. M. Baggio-Saitovitch, S. K. Xia, J. Magn. Magn. Mater. **110** 106-112 (1992)
[3] E. M. Baggio Saitovitch, J. Terra and F. J. Litterst, Phys. Rev. B **39**, 6403 (1989).
[4] C. Peng, S. Zhang, G. Li, D. Dai, J. Appl. Phys. **76**, 998 (1994).
[5] J. A. Gómez, S.K. Xia, E. C. Passamani, B. Giordanengo and E. M. Baggio-Saitovitch, J. Magn. Magn. Mater., **223** 112-118 (2001).
[6] G. Longworth and R. Jain, J. Phys. F: Met. Phys. **8**, 993-1007 (1978)
[7] G. Marest, H. Jaffrezic, J. Stanek, and H. Bineczycka, Nucl. Instrum. Methods Phys. Res. B **80-81**, 357 (1993)
[8] P. Steiner and S. Hüfner, Phys. Rev. B **12**, 842 (1975)
[9] N. Kataoka, K. Sumiyama and Y. Nakamura, J. Phys. F: Met. Phys. **18**, 1049-1056(1988).

[10] M. M. Pereira de Azevedo *et. al.*, J. Magn. Magn. Mater., **173**, 230-240 (1997).

[11] G. Rollmann, P. Entel, S. Sahoo, Comp. Mat. Sci. 35, 275 (2006)

[12] D. Altbir, J. d'Albuquerque e Castro, P. Vargas, Phys. Rev. B 54, R6823 (1996)

[13] D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, Phys. Rev. Lett. **61**, 2129 - 2132 (1988).

[14] D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, Phys. Rev. Lett. **62**, 316 (1989).

[15] M. Hanson, J. Phys. F: Met. Phys. 7, 2555 (1977)

[16] S.N. Mishra, P. Taneja, P. Ayyub, A. A. Tulapurkar, Phys. B, **312-313**, 162-164 (2002).

[17] A. Crépieux and C. Lacroix, Phyisica B **259-261**, 204-205 (1999).

[18] A. Crépieux and C. Lacroix, Phys. Rev. B **59**, 13824 (1999).

[19] U. Larsen, Phys. Rev. B **14**, 4356 (1976)

[20] M. G. Vavilov, L.I. Glazman, and A.I. Larkin, Phys. Rev. B **68**, 075119 (2003).

[21] J. S. Schilling, P. J. Ford, U. Larsen, and J. A. Mydosh, Phys. Rev. B **14**, 4368 (1976)